DATA QUALITY SUMMARY REPORT FOR NO/NO_Y DATA COLLECTED BY SONOMA TECHNOLOGY, INC., DURING THE CALIFORNIA REGIONAL PM_{10}/$PM_{2.5}$ AIR QUALITY STUDY

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1. INTRODUCTION AND OBJECTIVES

The purpose of this Data Quality Summary Report is to provide data users with an understanding of the quality of nitrogen oxide (NO) and reactive oxides of nitrogen (NO_y) data collected by Sonoma Technology, Inc. (STI) for the California Regional $PM_{10}/PM_{2.5}$ Air Quality Study (CRPAQS). **Tables D-1 and D-2** summarize the operating sites and times for NO/NO_y concentration measurements during CRPAQS. NO_y measurements were available from both NO/NO_y instruments and nitric acid instruments. This report provides summary information on data completeness, lower quantifiable limit (LQL), accuracy, and precision. NO/NO_y concentrations were measured with 1-minute time resolution and averaged to 5-minute and 60-minute values; only these latter values were reported in the corresponding database and reports. Data completeness and LQL were calculated for both data sets, while accuracy and precision were calculated using nightly NO calibration data and are applicable to both 5-minute and 60-minute data. Data completeness was calculated for all sites based on data delivered to ARB; the start date/time indicates the beginning of valid data, continuous until the stop date/time. Data validation suggested that all NO/NO_y instruments performed similarly; thus, Angiola was used as a representative site to calculate LQL, accuracy, and precision for all NO/NO_y monitors operated by STI in the study.

Table D-1. Location and duration of NO/NO_y instrument measurements made by STI during CRPAQS.

Site	Start Date/Time	Stop Date/Time
Angiola Trailer	02/09/00 00:00 PST	02/05/01 5:55 PST
Angiola 100-m Tower	12/05/00 00:00 PST	02/05/01 00:00 PST
Bakersfield	02/25/00 17:00 PST	02/15/01 23:55 PST
Bethel Island	11/18/00 15:00 PST	02/04/01 16:50 PST
Sierra Nevada Foothills	11/24/00 00:00 PST	02/06/01 10:15 PST

Table D-2. Location and duration of NO_y measurements made by STI using the nitric acid instrument during CRPAQS.

Site	Start Date/Time	Stop Date/Time
Angiola Trailer	12/13/00 00:00 PST	2/4/01 23:55 PST
Sierra Nevada Foothills	12/1/00 18:40 PST	2/15/01 12:55 PST

Several other documents are available from which to obtain information about the CRPAQS field study and data processing. Sampling locations are described in Wittig et al. (2003). Quality control screening procedures are summarized by Hafner et al. (2003). Results of systems and performance audits and intercomparisons are provided by Bush et al. (2001).

The data quality objectives (DQOs) for NO and NO_y, in accordance with the CRPAQS Quality Integrated Work Plan (QIWP) (1999), are shown in **Tables D-3a and D-3b**.

Table D-3a. Data quality objectives for NO data collected during CRPAQS.

Data Quality Metric	CRPAQS Objective
Completeness	90%
Lower Quantifiable Limit	0.02 ppb
Accuracy	0.05 ppb or 10%
Precision	0.02 ppb

Table D-3b. Data quality objectives for NO_y data collected during CRPAQS.

Data Quality Metric	CRPAQS Objective
Completeness	90%
Lower Quantifiable Limit	0.2 ppb
Accuracy	0.2 ppb or 10%
Precision	0.2 ppb

2. DATA COMPLETENESS

Data completeness for 5-minute and 60-minute NO and NO_y data are shown in **Tables D-4 through D-6**. Data capture quantifies the percentage of total records received versus the number expected during the "period of operation" defined by the start and stop dates/times in Tables D-1 and D-2; the start date/time is the first instance of valid data, and the period of operation is continuous until the stop date/time. The number of valid data points is divided by the number of captured data points to calculate the data recovery. Validity is defined for this calculation as any data point that has a quality control flag of V0 (valid) or V1 (valid but comprised wholly or partially of below-MDL data). Details of data validation are included in Hafner et al. (2003).

Table D-4. Data completeness values for NO at each site.

Monitoring Site	No. of Total Records	Expected No. of Records	Percent Capture[a]	No. of Valid Records	Percent Recovery[b]	No. of Suspect Records	No. of Invalid Records	No. of Missing Records
Angiola Trailer (5-min)	104,328	104,328	100	79,868	77	2882	16,402	5176
Angiola Trailer (60-min)	8694	8694	100	7118	82	374	801	401
Angiola 100-m Tower (5-min)	17,857	17,857	100	17,321	97	0	422	114
Angiola 100-m Tower (60-min)	1489	1489	100	1447	97	0	36	6
Bakersfield (5-min)	102,612	102,612	100	83,813	82	1858	16,691	250
Bakersfield (60-min)	8551	8551	100	7595	89	171	781	4
Bethel Island (5-min)	22,487	22,487	100	11517	51	7348	3539	83
Bethel Island (60-min)	1874	1874	100	1047	56	646	180	1
Sierra Nevada Foothills (5-min)	21,436	21,436	100	16,688	78	1733	3010	5
Sierra Nevada (60-min)	1787	1787	100	1491	83	147	149	0

[a] % of capture = total number of records/expected records*100%
[b] % recovery = number of valid records/total number of records

All sites had a 100% data capture rate for NO. Data recovery rates ranged from 51% (Bethel Island, 5-minute) to 97% (Angiola 100-m Tower). For the period December 13-17, 2000, the Bethel Island NO/NO_y instrument had numerous operational problems and data were invalidated. For November 18 through December 20, 2000, the nightly calibration system at Bethel Island was not plumbed properly to adequately document instrument performance on a daily basis; data were flagged as suspect. The Angiola Tower data recovery rate met the CRPAQS DQO; the data recovery rates for other sites did not.

Table D-5. Data completeness values for NO_y from the NO/NO_y instrument at each site.

Monitoring Site	No. of Total Records	No. of Expected Records	Percent Capture[a]	No. of Valid Records	Percent Recovery[b]	No. of Suspect Records	No. of Invalid Records	No. of Missing Records
Angiola Trailer (5-min)	104,328	104,328	100	78,417	75	4093	16,642	5176
Angiola Trailer (60-min)	8694	8694	100	7118	82	374	801	401
Angiola 100-m Tower (5-min)	17,857	17,857	100	17,321	97	0	422	114
Angiola 100-m Tower (60-min)	1489	1489	100	1447	97	0	36	6
Bakersfield (5-min)	102,612	102,612	100	83,510	81	1859	16,993	250
Bakersfield (60-min)	8551	8551	100	7568	89	172	807	4
Bethel Island (5-min)	22,487	22,487	100	11,519	51	7346	3539	83
Bethel Island (60-min)	1874	1874	100	1048	56	645	180	1
Sierra Nevada Foothills (5-min)	21,436	21,436	100	16,697	78	1734	3000	5
Sierra Nevada Foothills (60-min)	1787	1787	100	1492	83	147	148	0

[a] Percent capture rate (total number of records/expected records*100%)
[b] Percent recovery rate (=number of valid records/total number or records)

All sites had a 100% data capture rate. The data recovery rate ranged from 51% (Bethel Island, 5-minute) to 97% (Angiola 100-m Tower). For the period December 13-17, 2000, the Bethel Island NO/NO_y instrument had numerous operational problems and data were invalidated. For November 18 through December 20, 2000, the nightly calibration system at Bethel Island was not plumbed properly to adequately document instrument performance on a daily basis; data were flagged as suspect. The Angiola Tower data recovery rates met the CRPAQS DQO; the recovery rates at the other sites did not.

Table D-6. Data completeness values for NO_y from the nitric acid instrument at each site.

Monitoring Site	Total No. of Records	No. of Expected Records	Percent Capture[a]	No of Valid Records	Percent Recovery[b]	No of Suspect Records	No. of Invalid Records	No. of Missing Records
Angiola Trailer (5-min)	15,552	15,552	100%	11,382	73%	1647	2409	114
Angiola Trailer (60-min)	1296	1296	100%	1008	78%	150	132	6
Sierra Nevada Foothills (5-min)	21,809	21,820	100%	18,213	84%	0	3577	19
Sierra Nevada Foothills (60-min)	1819	1819	100%	1649	91%	0	170	0

[a] Percent capture rate = total number of records/expected records*100%
[b] Percent recovery rate =number of valid records/total number or records

Both the Angiola and Sierra Nevada Foothills sites had a 100% data capture rate. Data recovery rates ranged from 73% (Angiola, 5-minute) to 91% (Sierra Nevada Foothills, 60-minute). The 60-minute average data for Sierra Nevada Foothills met the CRPAQS DQO, the other data sets did not.

3. LOWER QUANTIFIABLE LIMIT

The LQL is the lowest concentration in ambient air that can be measured when processing actual samples. Sources of variability that influence the monitored signal at low concentrations include instrument noise and atmospheric variability. As a measure of this variability, two times the standard deviation of selected 5-minute and 60-minute data was used to estimate the LQL for the 5-minute and 60-minute data, respectively. The selected data were collected during relatively stable periods with concentrations close to zero. This is a conservative estimate of the LQL because it includes the concentration variability of the ambient air. Twelve consecutive data values were used to compute the LQL with the 5-minute data and six data values with the 60-minute data; atmospheric variation generally becomes too great after six hours to calculate a reasonable LQL. Because only half the number of data values were used in the calculation (see "N" in Equation D-1), the 60-minute LQL is expected to be higher than the 5-minute LQL, despite the "smoothing" that occurs when averaging 5-minute to 60-minute values.

The LQL is calculated as shown in Equation D-1. **Table D-7** shows the LQL for the sampling period, as well as the specific data strings used to calculate the LQLs. Only the 5-minute NO LQL meets the CRPAQS DQO.

$$\text{LQL} \approx 2s = 2\sqrt{\frac{\sum (NO - \overline{NO})^2}{N-1}} \qquad \textbf{(D-1)}$$

where:

$\overline{NO}$ = mean NO or NO_y concentration
N = number of measurements
σ = standard deviation

Table D-7. Time period used to calculate LQL, the LQL, and the corresponding mean concentration during the selected time period.

Type of data	Time Period Used in LQL Calculation	LQL (ppb)	Mean (ppb)
5-minute NO	10/25/00 21:40 – 22:40 PST	0.02	0.11
60-minute NO	5/8/00 09:00 – 15:00 PST	0.24	1.04
5-minute NO_y	9/22/00 21:40 – 22:40 PST	0.11	0.7
60-minute NO_y	5/8/00 09:00 – 15:00 PST	0.24	1.04

4. ACCURACY

The accuracy of NO/NO_y measurements can be evaluated using the deviation of measurements from a standard reference. This method quantifies the variability in the routine accuracy of the instrument by evaluating the span checks, which were performed nightly during CRPAQS.

Span checks were performed nightly at 90 ppb NO using the on-site calibrator. These nightly checks can be used to evaluate the accuracy of the instrument throughout the study. Accuracy can be expressed in terms of the 95% confidence interval (CI). For STI's NO/NO_y measurements, the 95% CIs were calculated from the differences between monitor response and known concentrations provided by the automatic span checks during routine operation. The 95% CI approximates the accuracy of the data as shown in Equation D-2.

$$\text{Accuracy} \approx 95\%\ \text{confidence interval} = 1.96\left(\frac{s_{span}}{\sqrt{N}}\right) \qquad \textbf{(D-2)}$$

where:

$$s_{span} = \sqrt{\frac{\sum (x - \bar{x})^2}{N-1}}$$

$$x = [\text{NO}]_{\text{cal}} - [\text{NO}]_{\text{measured}}$$

$$\bar{x} = \frac{\sum ([\text{NO}]_{\text{cal}} - [\text{NO}]_{\text{measured}})}{N}$$

$[NO]_{cal}$ = NO concentration output by the calibrator

$[\text{NO}]_{\text{measured}}$ = NO or NO_y corrected concentration measured by the analyzer.

Generally, one 5-minute average of span check data was obtained each night. A small number of span checks was eliminated because the instrument or the calibrator malfunctioned; only span checks of 90 ppb NO were utilized. The 95% CI and the number of nightly average span values used to estimate the CIs for NO/NO_y at Angiola are provided in **Table D-8**. The accuracy computed using span check data does not meet the CRPAQS DQO.

Table D-8. Accuracy at 90 ppb NO and number of span check data points used for the 5-minute NO and NO_y concentrations at the representative site, Angiola.

Parameter	No. of Spans Used	Accuracy at 90 ppb NO
NO	320	0.5 ppb
NO_y	320	0.5 ppb

5. PRECISION

The consistency of the nightly span concentrations provides a measure of precision in the NO/NO_y analyzer measurements. The precision was evaluated by comparing the measured concentration during the span check to the average measured concentration during span checks for the entire study. A small number of span checks was eliminated because the instrument or the calibrator malfunctioned; only span checks of 90 ppb NO were utilized. The CI at a 95% confidence limit of the span measurements was used to estimate the precision of the data as shown in Equation D-3. This is applicable to both 5-minute and 60-minute data.

$$\text{Absolute Precision} \approx \text{CL} = 1.96 \times \frac{\sigma_{\text{measured}}}{\sqrt{N}} \qquad \textbf{(D-3)}$$

where:

$$\sigma_{\text{measured}} = \sqrt{\frac{\sum \left([NO]_{\text{measured}} - \left[\overline{NO}\right]_{\text{measured}} \right)^2}{N-1}}$$

All the NO/NO_y concentrations in Equation D-3 refer to the concentrations measured during the NO span checks. **Table D-9** shows the precision calculated for the representative site, Angiola. The precision of the NO/NO_y measurements do not meet the CRPAQS DQO.

Table D-9. Precision and the number of NO span measurements used to calculate the precision of the 5-minute NO and NO_y data at the representative site, Angiola.

Parameter	No. of Spans Used	Precision at 90 ppb NO
NO	320	0.5 ppb
NO_y	320	0.4 ppb

6. REFERENCES

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